

Appln. No. 10/706,202
Amdt. Dated November 29, 2005
Reply to Office Action of July 29, 2005

REMARKS

Applicants acknowledge receipt of the Office Action dated July 29, 2005, in which Claims 1-26 and 29-43 are rejected under 35 U.S.C. §102(b) as being unpatentable over U.S. Published Patent Application 2001/0031793 (hereinafter *Singleton*), and furthermore Claims 27 and 44 are rejected under 35 U.S.C. §103(a) as being unpatentable over *Singleton* in view of U.S. Patent No. 6,465,530 (hereinafter *Roy-Auberger*).

I. Status of the Claims

Claim 28 stands canceled. Claim 37 is now canceled.

Claims 29-33, 35, 38, 39 and 44 are currently amended. Amendment to Claim 30 covers additional embodiments to which the Applicants are entitled and are supported by originally-filed paragraph [0029]. Amendments to Claims 29 and 31 provide better antecedent basis in these claims in view of the amendments made in Claim 35 from which they ultimately depend. Amendments to Claims 32, 33, 38, 39, and 44 changed the dependency of these claims to Claim 35.

Claims 1-27, 29-36 and 38-44 are pending.

II. Rejection of Claims Under 35 U.S.C. § 102(b).

Applicants respectfully traverse the Examiner's rejection and submit that Claims 1-26, 29-36 and 38-43 are not anticipated by *Singleton*. Applicants submit that *Singleton* does not teach nor suggest all of the limitations of independent Claims 6 and 35 as there is not explicit or implicit teaching of the use of an aluminum modifying agent or the use of an element in the modifying agent with a specific atomic volume in the method of preparation of the catalyst support used in the process of the present claimed invention. Moreover, there is also no teaching, nor suggestion in *Singleton* that it would be desirable to solve the problem addressed by Applicants and to achieve Applicants' purpose in the present claimed invention.

Singleton teaches a Fischer-Tropsch catalyst comprising a γ -alumina support doped with lanthanum oxide, barium oxide, or a combination thereof, its method of use to make a cobalt catalyst suitable for reacting a synthesis gas in a slurry bubble reactor and a method of preparing this catalyst (see Abstract of *Singleton*). *Singleton* discloses that the addition of the dopant into the alumina

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structure is preferably effected by the co-hydrolysis of a dopant alkoxide with aluminum alkoxide before boehmite crystallization. Thus *Singleton* teaches that the dopant precursor is contacted with the aluminum alkoxide in dissolved form in an aqueous solution before a solid structure is formed (*Singleton* Page 3, paragraphs [0026], [0028] and [0030]). The positive effects that *Singleton* is seeking with such doping of the alumina catalyst support are improved thermal stability of the supported catalyst when it is subjected to repeated reaction-regeneration cycles (*Singleton* Page 2, paragraph [0015]; Page 3, paragraphs [0031] and [0032]), and mitigation of the detrimental effect of small amount of titanium present in alumina (*Singleton* Page 5, paragraph [0064]; Catalyst 4 in Table 1). Indeed, *Singleton* would like to minimize the impact of high temperature or repetitive cycles of heating for regeneration after reaction on the alumina surface area. Moreover, *Singleton* regards titanium to be an impurity, as its addition is incidental during the γ -alumina preparation from aluminum alkoxide (*Singleton* Catalysts 1-3 in Table 1; Page 5, paragraph [0060]), and *Singleton* does not regard titanium as a modifying agent as set forth in the present claimed invention.

Singleton does not anticipate Claim 6 and its dependent claims 1-5 and 7-26

With respect to *Singleton*'s teaching regarding the doping of alumina, *Singleton* only discloses that lanthanum oxide, barium oxide, or a combination thereof would provide a more thermally stable alumina support that he seeks. *Singleton* does not disclose or hint that cobalt may be used to provide greater thermal stability to the alumina support. *Singleton* clearly regards cobalt as the catalytic metal of the catalyst and not a modifying agent for the alumina support as set forth in the present invention. Moreover, *Singleton* suggests that the successive exposure of these catalysts to high temperatures can cause an undesirable encapsulation of cobalt particles (*Singleton* Page 2, paragraph [0015]), and one having ordinary skill in the art would presume that *Singleton* would not find desirable to 'bury' cobalt into the alumina structure.

Moreover, the dopant elements La, Ba disclosed by *Singleton* have an atomic volume of *ca.* 22.6 cm³/mol and *ca.* 37.9 cm³/mol respectively, as shown in Table I in the Appendix section (the atomic volume of La was disclosed in Table 4 of Applicants' specification as filed, and the same type of calculation based on atomic weight and density was used to obtain the atomic volume of Ba). Contrary to the Examiner's statement in Page 3 of the Office Action, the atomic volume of La is not less than 14 cm³/mol. In fact, the atomic volumes of La, Ba are well above the *upper limit of the atomic volume range* recited in Claims 6, 21 and 22. Furthermore, *Singleton* never mentions the

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atomic volume of the dopant as being an important property. Clearly, one of ordinary skill in the art would not be led by the teachings of this reference to select an element in the modifying agent for the alumina support material based on a specific range of atomic volume.

Furthermore, *Singleton's* dopant being in the form of La_2O_3 and BaO in the thermally stable doped alumina have a molecular volume of $50.1 \text{ cm}^3/\text{mol}$ and $26.8 \text{ cm}^3/\text{mol}$ respectively, as shown in Table II in the Appendix section (the molecular volume of La_2O_3 was disclosed in Table 5 of Applicants' specification as filed, and the same type of calculation based on molecular weight and density was used to obtain the molecular volume of BaO). The molecular volumes of La_2O_3 and BaO are greater than the molecular volume ($25.7 \text{ cm}^3/\text{mol}$) of aluminum oxide, contrary to what is recited in Claim 23 (the molecular volume of Al_2O_3 was disclosed in Table 5 of Applicants' specification as filed).

Not only does *Singleton* fail to teach or suggest the modifying agent to contain an element with a specific atomic volume, there is also no teaching nor suggestion that it would be desirable to 'dope' alumina to solve the problem addressed by Applicants in the present claimed invention and to achieve Applicants' purpose, i.e., obtain a hydrothermally stable alumina support. Indeed, *Singleton's* teaching differs from the present claimed invention with respect to the intended effect of the doped alumina as a support for the hydrocarbon synthesis catalyst support. As stated above, *Singleton* discloses two purposes for the doping of alumina derived from aluminum alkoxide: greater thermal stability and mitigation of the detrimental impact of incidental titanium impurity in alumina on the activity of cobalt supported catalyst. However, *Singleton* does not expressly or implicitly teach the addition of a 'dopant' to alumina for *enhancing the hydrothermal stability of the alumina support*, wherein the hydrothermal stability is defined by Applicants as a "property of resisting morphological and/or structural change in the face of elevated heat and water vapor pressure" (see paragraph [0008] of the Applicants' specification as filed). Applicants have disclosed that the hydrothermal stability of support and catalyst can be determined for example by using a steaming test, which comprises exposing a sample to water in an autoclave at a temperature of 225°C and a pressure of 375 psig (approximating the Fischer-Tropsch operating conditions) for 2 hours (see paragraph [0115] of the Applicants' specification as filed). Thus, hydrothermal conditions not only encompass high temperature but also *presence of steam*. However, there is no mention in *Singleton* that the formation of water vapor during Fischer-Tropsch synthesis has or could have a negative impact on the stability of the alumina support. Moreover, *Singleton* does not state that it would be

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desirable to address this issue of hydrothermal stability of the alumina support, and how one having ordinary skill in the art could do or should do to address it. To the extent that *Singleton* teaches the use of La_2O_3 and/or BaO in alumina for enhancing the *thermal* stability of the support and the supported catalyst, *Singleton* does not teach nor suggest the use of this dopant or other dopants in alumina in order to enhance the *hydrothermal* stability of the support, that is to say, in order to prevent *hydrothermal attack* of the support structure by steam (as vaporized water) under the high-pressure high-temperature hydrocarbon synthesis conditions.

Applicants argue that the disclosure of an added element which results in modifying a structure in order to achieve a desired effect or desired change on a property of the resulting structure does not *necessarily* teach the desirability of another effect or improvement in another property of the resulting structure, nor does it *necessarily* teach that this modification would have a *positive impact* on another property of the resulting structure; and nor does it *necessarily* teach that the effect or change on a property of the resulting structure would be beneficial regardless of the composition or atomic volume of the added element. In other words, *a dopant which is known to improve the thermal stability of an alumina support may not necessarily improve its hydrothermal stability*. For example, lanthanum oxide is regarded as a suitable dopant by *Singleton* for improving the thermal stability of alumina. To the contrary, Applicants have found that the modification of alumina with La does not provide sufficient hydrothermal stability to the modified alumina (see [0122], [123] and [125]; Figure 2 in Applicants' specification as filed). Thus, based on *Singleton* as a whole, one having ordinary skill in the art is completely without notice of this important *hydrothermal* effect on the alumina support and is not provided enough guidance how to address it.

In view of all the recitations in Claims 6 that are neither taught nor suggested expressly or implicitly by *Singleton*, and further in view of the lack of guidance from *Singleton* to arrive to the present invention for Applicants' intended purpose, Applicants argue that *Singleton* does not put the public in possession of the use of the Applicants' present claimed process of Claim 6. Applicants thus submit that *Singleton* does not explicitly or implicitly anticipate Claims 6 for the reasons stated above. Applicants respectfully request that the Examiner withdraws the § 102 rejection on Claim 6 and its respective dependent Claims 1-5 and 7-26.

Singleton does not anticipate Claim 35 and its dependent Claims 29-34, 36 & 38-43

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Applicants amended Claim 35 to include the following limitation "wherein the aluminum-modified alumina support is modified by at least one modifying agent comprising aluminum by applying a modifying agent precursor comprising an aluminum salt, an aluminum hydroxide, or mixtures thereof, to an alumina precursor."

Singleton only discloses that lanthanum oxide, barium oxide, or a combination thereof would provide a more thermally stable alumina support that he seeks. *Singleton* does not teach nor suggest the doping of alumina with aluminum and the use of *two of the starting ingredients comprising aluminum*, i.e., alumina precursor and modifying agent precursor, in making the doped alumina. *Singleton* provides only aluminum alkoxide as the precursor for the alumina structure in the support. Specifically, *Singleton* does not teach nor suggest that the alumina precursor may be a transition alumina as recited in Claim 32, or a gamma-alumina as recited in Claim 33. Moreover, *Singleton* does not disclose 'impregnation' as a mode for doping the alumina as recited in Claim 29, as *Singleton describes* a support preparation method comprising the co-hydrolysis of aluminum alkoxide and a dopant alkoxide in order to generate the doped alumina.

In view of all the recitations in Claim 35 that are neither taught nor suggested expressly or implicitly by *Singleton*, Applicants argue that *Singleton* does not put the public in possession of the use of the Applicants' present claimed process of Claim 35. Applicants thus submit that *Singleton* does not anticipate Claim 35 for the reasons stated above. Applicants respectfully request that the Examiner withdraws the § 102 rejection on Claim 35 and its respective dependent Claims 29-34, 36 and 38-44.

III. Rejection of Claims Under 35 U.S.C. § 103(a).

In the Office Action mailed on July 29, 2005, Claims 27 and 44 were rejected in the Office Action under 35 U.S.C. § 103(a) as being unpatentable over *Singleton* in view of *Roy-Auberger*. The Examiner has stated that the present claimed differs from *Singleton's* teachings in that *Singleton* does not teach the use of a calcination at temperature between 800 °C and 900 °C, and that the modification of alumina with an aluminum salt. The Examiner further states in Page 4 of Office Action that "it would have been *prima facie obvious* to one of ordinary skill in the art at the time for the invention was made to prepare the aluminum modified alumina by co-precipitating a mixture of silicic acid and aluminum nitrate and calcining it at a high temperature in order to improve the mechanical properties, especially when it is used in a slurry bubble column reactor".

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Applicants respectfully traverse the Examiner's obviousness rejection and submit that *Roy-Auberger* does not cure the deficiencies and missing elements in *Singleton*'s teachings.

As a whole, the secondary reference, *Roy-Auberger*, teaches a silica-alumina support suitable for supporting a catalyst which is used in hydrocarbon synthesis from synthesis gas. *Roy-Auberger* is mainly concerned with the mechanical stability of a particulate catalyst supported on the silica-alumina support, as the catalyst particles tend to disintegrate into smaller particles during operation (*Roy-Auberger* Col. 6 line 65 to Col. 7 line 1; Col. 5 lines 44-46; Col. 10 line 65 to Col. 11 line 19; Table 3). *Roy-Auberger* discloses several embodiments of a co-precipitation method (*Roy-Auberger* Col. 2 line 48-65; Col. 3 lines 4-25) which result in a silica-alumina support having an *improved mechanical strength* and further characterized by a relatively high degree of Si and Al homogeneities (see disclosure of 'micrometric', 'micronic', and 'nanometric' homogeneities in *Roy-Auberger* Col. 2 lines 40-42; Col. 4 lines 19-28; and the homogeneity measurement method in *Roy-Auberger* Col. 4 lines 59-65). *Roy-Auberger* relates the improved mechanical strength of the silica-alumina support to the presence of more substantial and a greater number of *interactions between the alumina and the silica* in the silica-alumina support which are created by specific calcination conditions after the co-precipitation step (*Roy-Auberger* Col. 2 lines 62-65; Col. 3 line 1-3). *Roy-Auberger* further suggests the desirability to add a small proportion of a 'stabilizing element' to the silica-alumina support, where the 'stabilizing element' is preferably added in the form of a soluble salt (*Roy-Auberger* Col. 3 lines 27-38) and wherein the stabilizing element is in the form of M_2O_3 in the support, where M is La, Pr, or Nd. However, *Roy-Auberger* does not state the purpose for this stabilization. A reasonable inference from *Roy-Auberger*'s teaching is that the stabilizing element M_2O_3 in the silica-alumina support is also used for the mechanical stability of the catalyst, since Catalyst D containing La in the silica-alumina support is tested for mechanical stability in a similar fashion as the other Catalysts A-C that do not contain a stabilizing element in their silica-alumina support.

The combination of Singleton with Roy-Auberger does not provide all of elements of Claim 27

Applicants respectfully traverse the Examiner's rejection of Claim 27 under § 103 as being unpatentable and submit that, contrary to MPEP section 2143, the Examiner has failed to make a

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prima facie case of obviousness in rejecting such claims in that the combination of the cited references cited by the Examiner fails to teach or suggest all of the elements recited in the rejected claims; and both references fail to address the problem Applicants are addressing.

Singleton fails as a primary reference for not teaching or suggesting all the limitations of Claim 6 and for *Singleton*'s lack of guidance to one having ordinary skill in the art to modify alumina with a modifying agent comprising an element of an atomic volume within a certain range to improve the hydrothermal stability of the alumina. *Roy-Auberger* also did not recognize the problem of hydrothermal stability that Applicants are addressing. For example, there is no mention in *Roy-Auberger* that the formation of water vapor during Fischer-Tropsch synthesis has or could have an impact on the stability of the silica-alumina support. Similarly to *Singleton*, *Roy-Auberger* never addresses the issue of hydrothermal stability of the support, and how one having of ordinary skill in the art could or should do to address it. To the extent that *Roy-Auberger* teaches the formation of *greater silica/alumina interactions* and the optional use of stabilizing element for enhancing *mechanical* stability of the silica-alumina support, *Roy-Auberger* does not teach nor suggest the use of the optional stabilizing element in silica-alumina in order to enhance the *hydrothermal stability of alumina*. Applicants therefore submit that the teaching by *Singleton* and *Roy-Auberger* of a positive impact of a dopant or stabilizing element added to a support for increasing a certain stability of a support and/or the supported catalyst (such as thermal stability; mechanical strength) does not necessarily teach a positive impact of the same dopant or stabilizing element or of other compounds added to alumina for the purpose of enhancing another stability of the support (such as hydrothermal stability).

Furthermore, *Roy-Auberger* did not recognize that the atomic volume of the element in the modifying agent may be important for stabilizing alumina. The optional stabilizing element La, Nd or Pr disclosed by *Roy-Auberger* to further enhance the mechanical strength of silica-alumina has an atomic volume of *ca.* 22.6 cm³/mol, *ca.* 20.6 cm³/mol and *ca.* 20.8 cm³/mol respectively, as shown in Table I in the Appendix section (the atomic volume of La was disclosed in Table 4 of Applicants' specification as filed, and the same type of calculation based on atomic weight and density was used to obtain the atomic volume of Nd and Pr). *Roy-Auberger* is clearly more interested in the presence of more substantial and a greater number of *interactions between the alumina and the silica* in the silica-alumina support which are created by specific calcination high temperature conditions

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after the co-precipitation step in order to generate a *mechanically stronger silica-alumina* support (Roy-Auberger Col. 2 lines 62-65; Col. 3 line 1-3). Thus, Roy-Auberger does not teach a silicon-modified alumina, and this difference in support structures is significant. One having ordinary skill in the art would construe from Roy-Auberger's disclosure that the formation of composite compounds comprising both Al and Si such as aluminum silicate (Al_2SiO_5) may in fact provide the stabilizing element that renders the silica-alumina support more mechanically strong in Roy-Auberger. It should be noted that Al_2SiO_5 has a molecular volume of $51.5 \text{ cm}^3/\text{mol}$ as shown in Table II in the Appendix section, which is well above that of aluminum oxide.

Applicants respectfully disagree with the rationale of the obviousness rejection for at least the reasons stated above, and submit that a *prima facie* case was not properly set forth for Claim 27. Applicants respectfully request the withdrawal of the 103(a) rejection on Claim 27.

The combination of Singleton with Roy-Auberger does not provide all of elements of claim 44

Applicants respectfully traverse the Examiner's rejection of Claim 44 under § 103 as being unpatentable and submit that the combination of the references cited by the Examiner fails to teach or suggest all of the elements recited in the current claim 44 as it fails to suggest or teach all of the limitations of Claim 35 from which Claim 44 depends. Applicants submit that, similarly to Singleton, Roy-Auberger does not teach nor suggest that *two of the starting ingredients*, i.e., alumina precursor and modifying agent precursor, in making the aluminum-modified alumina. Roy-Auberger provides one aluminum-containing compound as the precursor for the alumina and a silicon precursor for making a silica-alumina support, and not an alumina support.

Applicants submit that a *prima facie* case was not properly set forth for Claim 44. Applicants respectfully request the withdrawal of the 103(a) rejection for Claim 44.

V. Conclusion

In conclusion, Applicants submit that all pending Claims 1-27, 29-36 and 38-44 are patentable over the applied art, and their allowance is respectfully solicited.

In this Response, Applicants may have at times referred to claim limitations in shorthand fashion, or may have focused on a particular claim element. This discussion should not be interpreted to mean that the other limitations can be ignored or dismissed. The claims must be

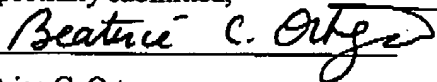
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viewed as a whole, and each limitation of the claims must be considered when determining the patentability of the claims. Moreover, it should be understood that there may be other distinctions between the claims and the prior art, which have yet to be raised, but which may be raised in the future. No new matter is introduced by this Response.

This is believed to be a full and complete response to the Office Action of July 29, 2005, as Applicants believe they have addressed the issues raised in the Office Action. Should Applicants not have properly understood the Office Action to which this Response is filed, or there is any remaining issue which the Examiner believes would possibly be resolved by a conversation, the Examiner is invited to call the undersigned at (281) 293-4751 so that further delay in a Notice of Allowance can be avoided.

Should any fees have been inadvertently omitted, or if any additional fees are required or have been overpaid, please appropriately charge or credit those fees to Deposit Account Number, 16-1575 of ConocoPhillips Company, Houston, Texas and consider this a petition for any necessary extension of time.

Respectfully submitted,



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APPENDIX

TABLE I lists the molecular weight, density and atomic volumes for the following elements: Al, Co, Si, La, Ba, Nd, and Pr that can be used to modify alumina. Atomic volumes of the elements are calculated as the ratio of the element atomic weight by the element density

Element	Characteristics of Elements		
	Atomic weight, g/mol	Density, cm ³ /g	Atomic volume, cm ³ /mol
Al	26.982	2.70	10.0
Co	58.933	8.86	6.65
Si	28.086	2.33	12.06
La	138.91	6.15	22.59
Ba	137.33	3.62	37.94
Nd	144.24	7.01	20.58
Pr	140.91	6.77	20.80

TABLE II lists the molecular weight, density and 'molecular' volumes of stabilizer elements for the following oxides of these elements: Al, Co, Si, La, Ba, Nd, and Pr, and aluminum silicate that may be formed during the preparation of the catalyst supports.

Stabilizing element	Characteristics of stabilizing elements		
	Molecular weight, g/mol	Density, cm ³ /g	Molecular volume, cm ³ /mol
Al ₂ O ₃	101.96	3.97	25.7
CoO	74.93	6.44	11.64
SiO ₂	60.09	2.65	22.7
La ₂ O ₃	325.8	6.51	50.1
BaO	153.33	5.72	26.8
Nd ₂ O ₃	336.48	7.24	46.5
Pr ₂ O ₃	309.81	6.90	47.8
Al ₂ SiO ₅	162.05	3.145	51.5

The atomic weight, molecular weight, and density of the elements used in Tables I and II can be found in CRC Handbook of Chemistry and Physics, 81st Edition, D.R. Lide, Ed., CRC Press, Inc., 2000-2001, page 4-39 for Al; page 4-40 for Al₂O₃; page 4-54 for Co; page 4-55 for CoO; page 4-84 for Si; page 4-85 for SiO₂; page 4-66 for La and La₂O₃; page 4-44 for Ba; page 4-45 for BaO; page 4-74 for Nd and Nd₂O₃; page 4-81 for Pr and Pr₂O₃; and page 4-40 for Al₂SiO₅.